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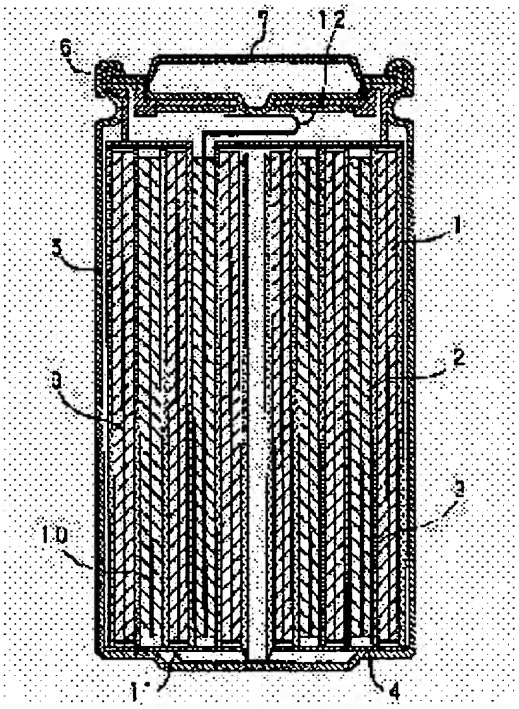
(54) NONAQUEOUS ELECTROLYTIC SECONDARY BATTERY

(57)Abstract:

PURPOSE: To provide a battery excellent in cycle characteristic with low internal resistance in which the oxidation resistance of a conductive agent is improved by adding a specified quantity of boron-contained graphite as the conductive agent in a positive electrode mix.

CONSTITUTION: In a nonaqueous electrolytic secondary battery having a positive electrode 1, a negative electrode 2, and a separator 3, a positive electrode mix is formed of a lithium composite oxide forming a positive electrode active material, a conductive agent, and a binder. As a conductive agent, 2-16wt.% of boron-contained graphite is contained in the positive electrode mix. The boron-contained graphite is oxidation resistant and difficult to oxidize under high potential. When the content of the boron-contained graphite is too small, sufficient conductivity is not imparted, and when it is too much, the active material filling quantity of the positive electrode 1 is reduced to loose the battery capacity.



LEGAL STATUS

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* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] Especially this invention relates to amelioration of the electric conduction agent used for a positive electrode about a nonaqueous electrolyte rechargeable battery.
[0002]
[Description of the Prior Art] The remarkable advance of an electronic technique in recent years is realizing small and lightweight-ization of electronic equipment one after another. In connection with it, it is called for also from the cell as a power source for migration that they are small, a light weight, and a high energy consistency increasingly.
[0003] Conventionally, as a rechargeable battery of a general application, water-solution system rechargeable batteries, such as a lead cell and a nickel cadmium battery, are in use. However, although these water-solution system rechargeable batteries are excellent in a cycle property, it cannot be said to be what can fully be satisfied in respect of cell weight or energy density.
[0004] Then, research and development of the nonaqueous electrolyte rechargeable battery which uses a dope and the matter which can be dedoped as a negative-electrode active material for a lithium ion like a carbonaceous ingredient for a lithium or a lithium alloy pan, and uses lithium multiple oxides, such as a lithium cobalt multiple oxide, as positive active material are performed briskly recently. This cell has high cell voltage and has a high energy consistency. If a carbonaceous ingredient is especially used for a negative-electrode active material, a cycle property will be improved and it will become practical as a supply power source of small and lightweight electronic equipment.
[0005] When using this nonaqueous electrolyte rechargeable battery with a cylindrical shape, an electrode is made into rolled electrode object structure from the point of securing reaction area. namely, the negative electrode which consists of carbonaceous ingredient powder with which this rolled electrode object serves as a negative-electrode active material, and a binder -- the band-like negative electrode which makes it come to hold a mixture to a negative-electrode charge collector, and the positive electrode which consists of the lithium multiple oxide, electric conduction agent, and binder used as positive active material -- the laminating of the band-like positive electrode which makes it come to hold a mixture to a positive-electrode charge collector is carried out through a separator, and it comes to wind it many times. in addition, a positive electrode -- a lithium multiple oxide is because it is the matter with electric resistance high itself comparatively, and he is trying for adding an electric conduction agent especially to a mixture to give conductivity to a positive electrode by adding conductive high artificial-graphite powder etc. as an electric conduction agent
[0006]
[Problem(s) to be Solved by the Invention] By the way, a nonaqueous electrolyte rechargeable battery has very high cell voltage as mentioned above. For this reason, it is required severely that an electrode should be excellent in conductivity.
[0007] However, the artificial graphite used as an electric conduction agent of a positive electrode until now has the fault of being inferior to oxidation resistance, oxidation arises under high potential, and

conductivity deteriorates. For this reason, by the cell using such an artificial graphite as an electric conduction agent of a positive electrode, in connection with the repeat of charge and discharge, internal resistance rose gradually, and the problem that a good cycle property is not acquired has arisen.
[0008] Then, this invention is proposed in view of such the conventional actual condition, the electric conduction agent excellent in oxidation resistance is gained, and internal resistance aims at offering the nonaqueous electrolyte rechargeable battery which was kept low and was excellent in the cycle property.

[0009]
[Means for Solving the Problem] in order to attain the above-mentioned purpose -- the nonaqueous electrolyte rechargeable battery of this invention -- a negative electrode -- a mixture and a positive electrode -- the nonaqueous electrolyte rechargeable battery which comes to have a mixture and nonaqueous electrolyte -- setting -- a positive electrode -- a mixture -- as an electric conduction agent -- a boron content graphite -- 2 - 16 % of the weight -- it is characterized by containing at a rate.
[0010] Moreover, the boron content of a boron content graphite is characterized by being 2.5 - 4 % of the weight by B-2O3 conversion.
[0011] this invention -- a negative electrode -- a mixture and a positive electrode -- it is applied to the nonaqueous electrolyte rechargeable battery which comes to have a mixture and nonaqueous electrolyte.

[0012] the above-mentioned positive electrode -- a mixture consists of for example, the lithium multiple oxide, electric conduction agent, and binder used as positive active material. Suppose that a boron content graphite is used as this electric conduction agent especially in this invention.
[0013] As for a boron content graphite, it comes to cover a graphite powder front face boron. Oxidation resistance is given by boron being put on the front face, such a graphite cannot oxidize easily under high potential, and good conductivity is maintained. Therefore, by the cell using such a boron content graphite as an electric conduction agent of a positive electrode, since an electric conduction agent maintains good conductivity as cell voltage is high, it will be maintained at low internal resistance and a good cycle property will be demonstrated.
[0014] What is graphite powder with a mean particle diameter of 50 micrometers or less, and holds boron 2.5 to 4% of the weight by B-2O3 conversion as a boron content graphite is desirable. Such a boron content graphite is obtained by grinding and classifying the graphite powder of trade name 2900RG for example, by the superior graphite company, or 9400RG so that it may become the above-mentioned mean particle diameter. In addition, as for the boron content graphite of 2900RG, boron processing is made by the natural graphite, and, as for the boron content graphite of 9400RG, boron processing is made by the granular graphite.
[0015] 2 - 16 % of the weight is suitable for the amount mixed to the positive electrode of this boron content graphite. Conductivity sufficient when there are too few amounts of a boron content graphite for a positive electrode is not given, but in many [too], the active material fill of a positive electrode decreases, and cell capacity is spoiled.
[0016] Although a boron content graphite is used as an electric conduction agent of a positive electrode as mentioned above in this invention, other components usually have each usable thing used with this kind of nonaqueous electrolyte rechargeable battery.
[0017] That is, as a lithium multiple oxide used as positive active material, a lithium cobalt multiple oxide, a lithium nickel multiple oxide, a lithium manganese multiple oxide, a lithium vanadium multiple oxide, etc. are mentioned, among these a lithium cobalt multiple oxide and a lithium nickel multiple oxide are desirable.
[0018] As an active material of a negative electrode, a dope / ingredient which can be dedoped is used in alkali ion. As such an ingredient, there are carbonaceous ingredients, such as a conductive polymer besides Li metal and a Li-aluminum alloy and corks polymer charcoal, for example, and a conductive polymer and a carbonaceous ingredient are desirable from the point of the formation of a long cycle life of a cell.
[0019] As nonaqueous electrolyte, what dissolved the lithium salt of LiPF6 grade in non-aqueous

solvents, such as propylene carbonate and ethylene carbonate, is used.
[0020]
[Function] this invention -- a positive electrode -- a boron content graphite is used as an electric conduction agent of a mixture. Oxidation resistance is given because boron contains, and this boron content graphite cannot oxidize easily under high potential, and maintains good conductivity. therefore, such a boron content graphite -- a positive electrode -- since an electric conduction agent maintains good conductivity as cell voltage is high, the nonaqueous electrolyte rechargeable battery used as an electric conduction agent of a mixture is maintained at low internal resistance, and demonstrates a good cycle property.
[0021]
[Example] The suitable example of this invention is explained based on an experimental result.
[0022] The nonaqueous electrolyte rechargeable battery produced by example 1 this example is shown in drawing 1 . In this example, it is the following, and such a nonaqueous electrolyte rechargeable battery was made and produced.
[0023] First, the band-like negative electrode 1 was produced.
[0024] After carrying out installation (oxygen bridge formation) of the functional group which contains oxygen for the petroleum pitch used as a start raw material ten to 20% of the weight, the carbonaceous ingredient which calcinated at the temperature of 1000 degrees C and had a property near glassy carbon was generated among the inert gas air current. This carbonaceous ingredient was ground and the negative-electrode active material was obtained by considering as powder with a mean particle diameter of 10 micrometers.
[0025] and the thing for which this carbonaceous ingredient powder 90 weight section and the polyvinylidene fluoride 10 weight section used as binding material are mixed -- a negative electrode -- a mixture is prepared and it distributes to N-methyl pyrrolidone -- making -- a negative electrode -- a mixture -- it considered as the slurry.
[0026] this negative electrode -- a mixture -- the band-like negative electrode 1 with the thickness of 170 micrometers, a width of face [of 41.5mm], and a die length of 280mm was produced by applying a slurry to both sides of copper foil with a thickness of 10 micrometers it is thin to the negative-electrode charge collector 9, and pressing it after desiccation.
[0027] Next, it is the following, and the band-like positive electrode 2 was made and produced.
[0028] LiCoO2 was generated by mixing by the mole ratio which becomes 1:2 and calcinating a lithium carbonate and cobalt carbonate at the temperature of 900 degrees C. And this LiCoO2 was ground and positive active material was obtained.
[0029] On the other hand, it considered as the mean particle diameter of 10 micrometers by grinding the boron content graphite of superior graphite company make and trade name 2900RG, and the electric conduction agent was obtained.
[0030] mixing with mixing percentage as shows the polyvinylidene fluoride used as LiCoO2 powder, the boron content graphite powder, and the binding material which were obtained in Table 1 -- a positive electrode -- a mixture is prepared and it distributes to N-methyl pyrrolidone -- making -- a positive electrode -- a mixture -- it considered as the slurry.
[0031] and this positive electrode -- a mixture -- the band-like positive electrode 2 with the thickness of 180 micrometers, a width of face [of 39.5mm], and a die length of 330mm was produced by applying a slurry to both sides of aluminum foil with a thickness of 20 micrometers it is thin to the positive-electrode charge collector 10, and pressing it after desiccation.
[0032] Thus, the rolled electrode object with an outer diameter of 13.0mm was produced by attaching the leads 11 and 12 for current collection in the band-like negative electrode 1 and the band-like positive electrode 2 which were produced, respectively, carrying out a laminating to them through the separator 3 made from polypropylene with a width of face [of 44mm], and a thickness of 25 micrometers, and winding around them many times. Subsequently, this rolled electrode object was inserted through the electric insulating plate 4 into the cell can 5 with an outer diameter [of 13.8mm], and a height of 50mm, and the nonaqueous electrolyte which dissolved LiPF6 in the mixed non-aqueous solvent with

which propylene carbonate and diethyl carbonate were further mixed by the capacity factor of 1:1 by the concentration of 1M was poured in. And the positive-electrode covering 7 was attached in this cell can 5 through the gasket 6, and the cell was produced with it.

[0033] example 2 - example 6 positive electrode -- a mixture -- it faced preparing a slurry and the cell was produced like the example 1 except having changed the mixing percentage of LiCoO2 powder, boron content graphite powder, and polyvinylidene fluoride, as shown in Table 1.

[0034]

[Table 1]

	ホウ素含有黒鉛（重量部）	$LiCoO_2$（重量部）	ポリフッ化ビニリデン（重量部）
実施例1	1	96	3
実施例2	2	95	3
実施例3	6	91	3
実施例4	10	87	3
実施例5	16	81	3
実施例6	20	77	3

[0035] example 1 of comparison - example of comparison 6 positive electrode -- a mixture -- it faced preparing a slurry, the artificial graphite (trade name KS-15) was used instead of the boron content graphite as an electric conduction agent, and the cell was produced like the example 1 except having mixed LiCoO2 powder, graphite powder, and polyvinylidene fluoride with the mixing percentage shown in Table 2.

[0036]

[Table 2]

	黒鉛（重量部）	$LiCoO_2$（重量部）	ポリフッ化ビニリデン（重量部）
比較例1	1	96	3
比較例2	2	95	3
比較例3	6	91	3
比較例4	10	87	3
比較例5	16	81	3
比較例6	20	77	3

[0037] About the cell produced as mentioned above in the example 1 - the example 6 and the example 1 of a comparison - the example 6 of a comparison, after charging on condition that 300mA of charging currents, and maximum electrical-potential-difference 4.2V, it discharged on condition that 18 ohms of load resistance, and cut-off voltage 2.75V, and capacity and internal resistance were measured. Moreover, it asked for the capacity maintenance factor [as opposed to a 100 times repeat deed and 1 cycle eye for a charge-and-discharge cycle] of a 100 cycle eye on the same conditions. The internal

resistance, the capacity, and the capacity maintenance factor which were measured are shown in Table 3 and Table 4.

[0038]

[Table 3]

	内部抵抗 (mΩ)	2.75V カットオフ容量 (mAh)	容量維持率 (%)
実施例 1	125	270	91
実施例 2	80	360	93
実施例 3	60	420	95
実施例 4	55	405	92
実施例 5	46	385	92
実施例 6	38	360	92

[0039]

[Table 4]

	内部抵抗 (mΩ)	2.75V カットオフ容量 (mAh)	容量維持率 (%)
比較例 1	150	250	85
比較例 2	100	350	86
比較例 3	70	400	88
比較例 4	60	380	86
比較例 5	55	370	85
比較例 6	50	350	85

[0040] When the case of the cell of the example 1 which used for the electric conduction agent the boron content graphite shown in Table 3 - an example 6 is compared with the case of the cell of the example 1 of a comparison which used for the electric conduction agent the artificial graphite which shows in Table 4 - the example 6 of a comparison and electric conduction doses are the same things, the direction of the cell of an example 1 - an example 6 has low internal resistance, and has become a value with a big cut-off capacity. Moreover, a capacity maintenance factor is also large. This shows that the boron content graphite is superior to an artificial graphite as an electric conduction agent.

[0041] moreover, the positive electrode of a boron content graphite -- since the amount of mixing to a mixture can make internal resistance low enough, and capacity and a capacity maintenance factor boil it markedly and it serves as a big value, it is understood that 2 - 16 % of the weight is desirable.

[0042] In addition, at this example, it is superior graphite company make to a boron content graphite. Although the case where trade name 2900RG was used was explained, also when 9400RG is used, it is checked that the result of this inclination is obtained.

[0043]

[Effect of the Invention] clear also from the above explanation -- as -- the nonaqueous electrolyte

rechargeable battery of this invention -- a positive electrode -- since a boron content graphite is used as an electric conduction agent of a mixture -- cell voltage is high -- a positive electrode -- it is possible for low internal resistance to be maintained and to acquire a good cycle property, without the conductivity of a mixture deteriorating.

[Translation done.]